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(54)【発明の名称】　高強度ポリエチレン繊維およびその製造方法

(57)【要約】
【課題】　温度変化に対する繊維特性の変化が極めて少なく室温での強度保持率の高い、各種用途に好適な高強度ポリエチレン繊維を提供することを可能とした。
【解決手段】　繊維状態での極限粘度［ηＦ］が５以上のエチレン成分を主体とするポリエチレン繊維であり、その強度が２０ｇ／ｄ以上、弾性率が５００ｇ／ｄ以上であり、かつその繊維の動的粘弾性の温度分散測定におけるγ分散の損失弾性率のピーク温度が－１１０℃以下であり、その損失正接が０．０３以下であることを特徴とする高強度ポリエチレン繊維。

【特許請求の範囲】

【請求項１】繊維状態での極限粘度［η］が５以上のエチレン成分を主体とするポリエチレン繊維であり、その強度が２０ｇ／ｄ以上、弾性率が５００ｇ／ｄ以上であり、かつその繊維の動的粘弾性の温度分散測定におけるγ分散の損失弾性率のピーク温度が－１１０℃以下であり、さらに損失正接（tanδ）が０．０３以下であることを特徴とする高強度ポリエチレン繊維。

【請求項２】極限粘度［η］が５以上でありかつ、その重量平均分子量と数平均分子量との比（Ｍｗ／Ｍｎ）が４以下であるエチレン成分を主体とする高分子量重合体（Ａ）を９９重量部乃至５０重量部、高分子量重合体（Ａ）に対して少なくとも１．２倍の極限粘度を有する超高分子量重合体（Ｂ）を１重量部乃至５０重量部含有する重合混合物を、濃度が５重量％以上８０重量％未満となるように溶剤に溶解して後、紡糸、延伸することを特徴とする高強度ポリエチレン繊維の製造方法。

【請求項３】重合混合物の平均極限粘度［η］Mが１０以上でありかつ、得られた繊維の極限粘度［η］Fが次式で与えられることを特徴とする高強度ポリエチレン繊維の製造方法。

0.7×［η］M≦［η］F≦0.9×［η］M

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、各種ロープ、釣り糸、土木・建築等のネット・シート材、化学フィルターやセパレータ用の布帛・不織布、防弾チョッキを始めとする防護衣料やスポーツ衣料、あるいはヘルメットや耐衝撃性コンポジット，スポーツ用コンポジット用補強材、特に極低温から室温雰囲気で使用される各種産業用材料として、広範囲の用途に使用可能な高強度ポリエチレン繊維であり、温度変化の大きい環境下で使用される条件下でその性能の温度に対する変化、特に強度や弾性率などの力学特性において温度変化の少ない高強度ポリエチレン繊維および、それを工業生産に十分な速度にて製造する方法に関する。

【０００２】

【従来の技術】超高分子量ポリエチレンを原料にして高強度・高弾性率繊維を得ようとする試みは近年活発であり、非常に高い強度・弾性率を有する繊維が報告されている。例えば、特開昭５６－１５４０８号公報には、超高分子量ポリエチレンを溶剤に溶解し得られたゲル状の繊維を高倍率に延伸する、いわゆる「ゲル紡糸法」の技術が開示されている。

【０００３】「ゲル紡糸法」により得られた高強度ポリエチレン繊維は有機繊維として非常に高い強度・弾性率を有し、さらには耐衝撃性が非常に優れる事が知られており、各種用途においてその応用が広がりつつある。かかる高強度繊維を得る目的において、前出の特開昭５６－１５４０８号公報によれば、極めて高い強度と弾性率を有する素材を提供する事が可能であると開示されている。しかしながら一方で、高強度ポリエチレン繊維は温度による性能の変化が非常に大きいことで知られている。例えば、－１６０℃付近から温度を変化させてその引っ張り強度を測定すると、低温から温度上昇と共に徐々にその低下が観察され、特に－１２０℃～－１００℃付近においてその性能の低下が著しい。このような温度による性能の変化は本素材の温度変化の大きい環境下での使用を困難なものにするともに、逆に言えば極低温での物性が室温まで保持できれば従来の高強度ポリエチレン繊維の性能を飛躍的に向上させることが期待される。

【０００４】従来、このような高強度ポリエチレン繊維の温度変化に因る力学特性の変化を制御するこころみとして、特開平７－１６６４１４号公報に開示されているごとく、特定の分子量を持つ超高分子量ポリエチレン原料とその得られる繊維の分子量とを適正な範囲にすることで、－１００℃以下のいわゆる極低温領域での振動吸収性を向上させる試みが示唆されているが、基本的に当該技術においては極低温での力学分散を大きくする。つまり、むしろ弾性率の変化を大きくする試みであり、本発明の目指す、力学特性の低下を少なくする試みとは相反するものであった。

【０００５】又、特開平１－１５６５０８号公報や特開平１－１６２８１６号公報には上記のゲル紡糸法において過酸化物や紫外線照射などの手段により、高強度ポリエチレン繊維のクリープを低減する試みが開示されている。基本的に本手法によれば前述のγ分散の力学分散が低くなることが記され本発明の述べる好ましい方向ではあるが、両発明は高強度ポリエチレン繊維のクリープを改良するのが目的であり、力学特性の温度変化による変化を低減するものでは無かった。特に、通常γ分散における緩和強度が小さくなると、その緩和が起こる温度も高温にシフトするのが通例であり、従来の手法では本発明が目指すより温度の変化に対して力学特性の変化が少ないこと、すなわちγ分散温度はより低温に移行することが好ましいことからは逆の方向であった。

【０００６】特に、γ分散の温度を－１００℃以下の温度域に属するγ分散の値をその温度域は極低温に維持しながら緩和強度として小さくすることは、その極低温での高い物性(特に強度)が長く室温近傍でも緩和せずに維持されることを示唆し、そのような繊維の出現は極めて産業上の利用価値の大きい繊維と言えよう。又、後述するようにこのような新規な特性を有する繊維は従来の高強度ポリエチレン繊維として有するべき基本的特長を損なうことなく代替可能であるばかりか、その製造工程中、特に延伸工程においても高強度繊維でありながら極めて高速度で延伸することが期待できる。すなわち、優れた性能を有する高強度ポリエチレン繊維をより高い生産性で得る事ができる新規な製造方法としてもその産業上の意義がある。

【０００７】

【発明が解決しようとする課題】以上の観点に基づき、本発明は、常温で極めて優れた力学特性を有してかつ、広範囲での温度変化、特に液体窒素温度域における強度や弾性率などの力学特性が室温でも高いレベルで維持されたことを特徴とする高強度ポリエチレン繊維およびその新規な製造方法を提供することを目的とする。

【０００８】

【課題を解決するための手段】即ち本発明は、繊維状態での極限粘度［η］が５以上のエチレン成分を主体とするポリエチレン繊維であり、その強度が２０ｇ／ｄ以上、弾性率が５００ｇ／ｄ以上であり、かつその繊維の動的粘弾性の温度分散測定におけるγ分散の損失弾性率のピーク温度が－１１０℃以下であり、さらにその損失正接（tanδ）が０．０３以下であることを特徴とする高強度ポリエチレン繊維に関する。さらに本発明は、極限粘度［η］が５以上でありかつ、その重量平均分子量と数平均分子量との比（Ｍｗ／Ｍｎ）が４以下である、エチレン成分を主体とする高分子量重合体（Ａ）を９９重量部乃至５０重量部、高分子量重合体（Ａ）に対して少なくとも１．２倍の極限粘度を有する超高分子量重合体（Ｂ）を１重量部乃至５０重量部含有してなる重合混合物を、濃度が全量の５重量%以上８０重量%未満となるように溶剤に溶解して後、紡糸、延伸されることを特徴とする高強度ポリエチレン繊維の製造方法を提供し、さらにはその重合体混合物の平均極限粘度[η]Mが１０以上でありかつ、得られた繊維の極限粘度[η]Fが次式で与えられることを特徴とする超高強度ポリエチレン繊維の製造方法に関するものである。

0.7×[η]M≦ [η]F≦0.9×[η]M

【０００９】以下、本発明を詳述する。本発明における高分子量ポリエチレンとは、その繰り返し単位が実質的にエチレンであることを特徴とし、少量の他のモノマー例えばα－オレフィン，アクリル酸及びその誘導体，メタクリル酸及びその誘導体，ビニルシラン及びその誘導体などとの共重合体であっても良いし、これら共重合物どうし、あるいはエチレン単独ポリマーとの共重合体、さらには他のα－オレフィン等のホモポリマーとのブレンド体であってもよい。特にプロピレン，ブテン－１などのαオレフィンと共重合体を用いることで短鎖あるいは長鎖の分岐をある程度含有させることは本繊維を製造する上で、特に紡糸・延伸においての製糸上の安定を与えることとなり、より好ましい。しかしながらエチレン以外の含有量が増えすぎると反って延伸の阻害要因となるため、高強度・高弾性率繊維を得るという観点からはモノマー単位で５ｍｏｌ％以下、好ましくは１ｍｏｌ％以下であることが望ましい。もちろんエチレン単独のホモポリマーであっても良い。

【００１０】本発明の骨子は、繊維状態で測定の動的粘弾性特性の温度分散におけるγ分散の損失弾性率のピーク温度が－１１０℃以下、好ましくは－１１５℃以下であり、さらにその損失正接（tanδ）の値が０．０３以下好ましくは０．０２以下であることを特徴とする繊維を得ることにあり、また該特性を得た繊維を得てなお、従来と同種の繊維の製造方法よりも極めて優れた高い生産性、具体的には高速度で延伸可能な高強度ポリエチレンの製造方法を提供する。

【００１１】本発明の繊維の温度による性能の変化が少ないこと、特に室温での力学物性、特に強度に優れていることは。繊維の動的粘弾性のγ分散ピーク温度で定義することができる。すなわち、力学分散の起こる温度域では通常、弾性率の著しい低下が観察される。高強度ポリエチレン繊維の場合、通常－１００℃付近にγ分散が観察される。ポリエチレンはこのγ分散を境にして以後、室温へ向かって温度上昇とともに急激にその物性値が低下する。例えば、液体窒素等使った極低温雰囲気下（約－１６０℃）で４ＧＰａもの高強度を有するポリエチレン繊維を、室温で測定すると約３ＧＰａ程度まで強度が低下するという現象が見られた。このような性質は、広範囲の温度域で該繊維を使用しようする場合、各種製品設計上好ましくないことはもちろんであるが、逆にこの現象を改善できれば室温での強度を飛躍的に向上せしめることが可能となると考えられる。従って、繊維の使用温度域を広げる目的でγ分散の温度をより低温に維持してかつ、強度の温度による低下をふせぐべく、その値を低くすることは上記の目的に対して非常に有効である。

【００１２】かかる、材料の設計思想に基づき、新しい繊維の開発を目指す際にまず着目されるγ分散とは、繊維を構成している分子の側鎖や末端などの局所的な欠陥に由来するものであることが知られている。このような欠陥を低減すれば、γ分散の緩和強度すなわち損失正接（tanδ）を低下させることができるが、そうすると繊維の微細構造としてその完全度がより高くなり、γ分散の発生する温度はより高温へ自動的に移行するのが常であった。すなわち、γ分散のピーク温度を低温に維持したまま、その緩和強度を低減することは、従来技術においては相反する方向であり、到底到達することが出来ない領域であった。而して、本発明の提供する繊維のようにγ分散のピーク温度が逆に非常に低温に維持されてかつその値が非常に小さいことは従来常識からは、極めて驚くべきことである。

【００１３】さて本発明に係る繊維を得る手法は当然ながら新規でかつ慎重な製法で得ることができる。また、以下に述べる手法は本発明で提供する高強度ポリエチレン繊維が従来の高強度ポリエチレンの一般的な特徴を兼ね備えていることから、その非常に高い生産性を提供する新規な製法としても産業的な価値がある。

【００１４】すなわち本繊維は、前述の「ゲル紡糸法」が実際的手法とて有効であるが、超高分子量ポリエチレ

ンを成形して従来知られている高強度ポリエチレン繊維を得る手法であれば特に基本となる製糸技術は問わない。本発明においてまず重要なのは原料となるポリマーである。

【００１５】すなわち、本発明においては、極限粘度［η］が５以上でありかつ、その重量平均分子量と数平均分子量との比（Ｍｗ／Ｍｎ）が４以下である、エチレン成分を主体とする高分子量重合体（Ａ）を９９重量部乃至５０重量部、高分子量重合体（Ａ）に対して少なくとも１．２倍の極限粘度を有する超高分子量重合体（Ｂ）を１重量部乃至５０重量部含有する少なくとも２種類の超高分子量ポリエチレンの重合混合物を用いることが推奨される。この際、主となる重合体（Ａ）は極限粘度が５以上、好ましくは１０以上でありかつ、４０未満であり、かつポリマーをＧＰＣ（ゲル・パーミエーションクロマトグラフィー法）で測定したＭｗ／Ｍｎが４以下好ましくは３以下、さらにこのましくは２．５以下であることが望ましい。

【００１６】本発明のようなγ分散の温度が先ず低い値であるためには、分岐や末端などの欠陥部ができるだけ小さいものを選択することが肝要であり、その意味で主体となる重合体（Ａ）の重合度は重要であり、極限粘度が５未満では分子の末端が非常に大きくなりγ分散のtanδ値が大きくなってしまう。また４０を超えると逆に、製糸上溶液の粘度が上昇しすぎて製糸が困難となる。ここで、極限粘度で代替して表せられる平均的重合度と共にその分布、いわゆる分子量分布は非常に重要であり、ＧＰＣで測定したＭｗ／Ｍｎは４以下であることが望ましい。このような超高分子量でかつ分子量分布が比較的揃った原料を用いるとγ分散を低温に維持したまま、そのtanδの値を低くすることが容易となる。

【００１７】この理由は良く分からないが、分子鎖が引き揃えられた場合、伸びきり鎖で形成されていると推定される結晶は分子が整列して配向することで、結晶内部には分子末端が非常に少なくなり、分子の末端はいわゆる非晶部にまとまって留置されるのではないかと推定している。すなわち、本繊維の構造の大部分を占める結晶部はより完成度の高い欠陥の少ない結晶構造となり、非晶部に分子末端などの成分が集中するのではないか。そうであると、γ分散を支配する局所欠陥が、結晶内部に多く存在すると、そのピーク温度が高温へシフトすることが学術的には知られており、本発明にかかる繊維の結晶部に分子末端などの局所部が少ないという事実と符合するとみることが出来る。もともと、本発明にかかる繊維の主要構造は伸び切り鎖からなる結晶構造であるために非晶部分に分子末端が集中してもさほど物性に影響を与えないと推定されるが、以上は本発明の効果を説明するために考えられうる仮説であり、定かでは無い。

【００１８】このように、極く狭い分子量分布を持つ超高分子量ポリエチレン重合体は通常の紡糸手法に供するだけでは、原料重合体の分子量分布が非常に狭いことに由来して紡糸で安定して吐出できなかったり、吐出された溶液はほとんど延伸性が無くその成形は事実上不可能である。上述のポリマーを従来のゲル紡糸法に供与せしめるためには少なくとも分子量分布Ｍｗ／Ｍｎが４より大きいことが望ましい。かかる低分子量分布の重合体を利用する試みとして特開平９－２９１４１５号公報のごとく、粘度平均分子量３０万以上でＭｗ／Ｍｎが３以下の特殊な触媒により調整された超高分子量ポリエチレン系重合体を用いて高強度高弾性率繊維を得られた技術が開示されている。該公報に記載されているごとく、高強度ポリエチレン繊維を製造する一般的な製造法であるゲル紡糸法よりも、該開示技術はむしろポリマーを濃度０．２ｗｔ％以下の希薄溶液に溶解して得られる単結晶物集合体の乾燥試料から固相押出し法あるいはゲル延伸法を組み合せて製造されるのが一般的であると述べられ、実施例にも単結晶集合物を利用した技術が開示されている。この例のように、従来のゲル紡糸法にかかる低Ｍｗ／Ｍｎのポリマーを供して紡糸・延伸工程を経ることは非常に困難であった。また、該公報に開示の非常に希薄な溶液から作成されたゲル延伸フィルムの物性が、本発明の提供する新規な繊維とは性状および物性上も異なることは改めて述べるまでも無い。

【００１９】このような分子量分布が非常に狭い重合体が成形困難である理由は推定でしかないが、分子量分布が狭くなることで分子鎖の絡み合いが激減し、それにより紡糸や延伸の際に分子鎖を変形させるのに必要な応力を均一に伝播できなくなるからでは無いかと推定している。かかる観点に基づき、旧来の技術を改善するべく鋭意検討をした結果、主成分である重合体（Ａ）９９乃至50重量部に対してその極限粘度の少なくとも１．２倍の超高分子量重合体（Ｂ）を１重量部乃至５０重量部混合することで、著しく紡糸での曳糸性（紡糸口金を出た溶液を引き伸ばす場合の引き取りやすさ）や延伸のしやすさ、その速度が著しく向上することが判明し、得られた繊維もより前述に求めるごとき特性、すなわちγ分散温度が低くかつtanδが低くなることを見出し、本発明に到達した。さらに本発明においてこれら混合物のポリマーの平均極限粘度［η］Mが１０以上でかつ、その重合体が全量の５重量％以上８０重量％未満となるように溶剤に溶解して紡糸・延伸する際に得られた繊維の極限粘度［η］Fが次式となるように製造条件を工夫すると、さらに繊維を所望の物性に劇的に近づけることが可能となる。

【００２０】$0.7\times[\eta]M \leqq [\eta]F \leqq 0.9\times[\eta]M$

【００２１】このような、原料となるポリマー分子量と得られる繊維の関係がかかる繊維の物性とどのように係わるかは定かでは無いが、繊維の極限粘度［η］Fが［η］Mの90％の値を超えると、２つの分子量の異なるポリマーが均一に混合せず、延伸性が極めて不調となる、一方、

［η］Fが［η］Mの７０％の値未満であると、２種のポリマーを混合した効果がほとんど無くなり、結果としては分子量分布の通常通り広い高強度ポリエチレン繊維と同程度の物性しか得ることができない。このように原料のポリマーと得られ繊維の重合度の差が大きいことは、工程中で分子鎖が切断されていることを意味し、何らかの分子量分布の再調整が行われていることは必至である。その際、混合物の高分子量側のポリマーがより劣化される機会が多いと推定され、それゆえこの高分子量物がより低分子量物の分子量分布域を包括するように全体の分子量分布が調整ことにより、よりスムーズな分子配列を伴いながら、一方で依然残留する高分子量成分が成形時の張力を伝播する役目を担うことで、成形性と紡糸・延伸での加工性を両立したのではないかと推定しているが定かでは無い。

【００２２】上記製法等により得られた繊維は、繊維状態での極限粘度［η］Fが５以上、好ましくは１０以上、４０未満であり、その強度が２０ｇ／ｄ以上、好ましくは２５g/d以上,更に好ましくは３５g/d以上、また弾性率が５００ｇ／ｄ以上、好ましくは８００g/d以上,更に好ましくは１２００g/d以上であり、上述の力学分散特性との相乗効果により、実用面で従来にない極めて優れた特性を有するポリエチレン繊維を提供することを可能とした。

【００２３】

【実施例】以下に本発明における特性値に関する測定法および測定条件を説明する。

（動的粘弾弾性測定）本発明における動的粘度測定は、オリエンテック社製「レオバイブロンＤＤＶ－０１ＦＰ型」を用いて行った。繊維は全体として１００デニール±１０デニールとなるように分繊あるいは合糸し、各単繊維ができる限り均一に配列するように配慮して、測定長（鋏金具間距離）が２０ｍｍとなるように繊維の両末端をアルミ箔で包みセルロース系接着剤で接着する。その際の糊代ろ長さは、鋏金具との固定を考慮して５ｍｍ程度とする。各試験片は、２０ｍｍの初期幅に設定された鋏金具（チャック）に糸が弛んだり捩じれたりしないように慎重に設置され、予め６０℃の温度、１１０Hzの周波数にて数秒、予備変形を与えてから本実験を実施した。本実験では－１５０℃から１５０℃の温度範囲で約１℃／分の昇温速度において１１０Ｈｚの周波数での温度分散を低温側より求めた。測定においては静的な荷重を５ｇｆに設定し、繊維が弛まない様に試料長を自動調整させた。動的な変形の振幅は１５μｍに設定した。

【００２４】（強度・弾性率）本発明における強度，弾性率は、オリエンティック社製「テンシロン」を用い、試料長２００ｍｍ、伸長速度１００％／分の条件で歪一応力曲線を雰囲気温度２０℃、相対湿度６５％条件下で測定し、曲線の破断点での応力を強度（ｇ／ｄ）、曲線の原点付近の最大勾配を与える接線より弾性率（ｇ／ｄ）を計算して求めた。なお、各値は１０回の測定値の平均値を使用した。

【００２５】（極限粘度）１３５℃のデカリンにてウベローデ型毛細粘度管により、種々の希薄溶液の比粘度を測定し、その粘度の濃度にたいするプロットの最小２乗近似で得られる直線の原点への外挿点より極限粘度を決定した。測定に際し、原料ポリマーのがパウダー状の場合はその形状のまま、パウダーが塊状であったり糸状サンプルの場合は約５ｍｍ長の長さにサンプルを分割または切断し、ポリマーに対して１ｗｔ％の酸化防止剤（商標名「ヨシノックスＢＨＴ」吉富製薬製）を添加し、１３５℃で４時間撹はん溶解して測定溶液を調整した。

【００２６】（分子量分布測定）本特許におけるＭｗ／Ｍｎはゲル・パーミエーションクロマトグラフィー法にて測定した。用いた装置はＷａｔｅｒｓ社製（１５０ＣＡＬＣ／ＧＰＣ）とカラムとして東ソ（株）製(ＧＭＨＸＬｼﾘｰｽﾞ)を用い１４５℃の温度で測定した。分子量の検量線はＰｏｌｙｍｅｒ　Ｌａｂｏｒａｔｏｉｅｓ社製（Polystyren-High Molecular Weight Calibration Kit)を用いて作成した。試料溶液は、トリクロルベンゼンに０．０２ｗｔ％となるようにポリマーの０．２ｗｔ％にあたる酸化防止剤(チバガイギー(社)製Irgafos168)を添加して１４０℃で約８時間溶解したものを用いた。

【００２７】以下、実施例をもって本発明を説明する。

（実施例１）極限粘度が１８．５でかつその分子量分布指数Ｍｗ／Ｍｎ＝２．５の超高分子量ポリエチレンのホモポリマー（Ａ）を９９重量部と極限粘度が２８．０でかつその分子量分布が約Ｍｗ／Ｍｎ＝５．５のポリマー（Ｄ）を２重量部加えたパウダー状の混合物が全量の３０重量％となるようにデカヒドロナフタレン７０重量％を常温で添加した。この際、重合物混合物の極限粘度［η］Mは１８．８であった。この混合重合体のデカリン分散体を２軸型の混合押し出し機に供給し、２００℃の温度条件および１００ｒｐｍで溶解・押し出しを実施した。尚この際、酸化防止剤は使用しなかった。

【００２８】このようにして調整された溶液は０．６ｍｍ直径を有するオリフィスが４８ホール設置された口金を用いて各ホールの吐出量が１．２g/minとなるように押し出して後、直ちに室温に調整した不活性ガスにて溶剤を一部除去しつつ冷却し、９０m/minの速度で引き取りを実施した。引き取り直後のゲル状の繊維のポリマー含有量は５５重量％であった。この引き取られた糸は直ちに１２０℃のオーブンにて４倍延伸されて後、一旦巻き取り、さらに１４９℃に調整されたオーブンにて４．５倍に延伸されて高強度繊維を得た。得られた繊維の動的粘弾性特性を含む諸物性を表１に示す。

【００２９】（実施例２）実施例１における主成分ポリマーとして極限粘度が１２．０のポリマーを用いた他は、同様の操作で延伸糸を得た。この際、重合物混合物の極限粘度［η］Mは１０．６であった。実施例１に比

べ、延伸が非常にスムーズであったが、得られた繊維の強度は若干低下した。

【００３０】（実施例３）実施例１の主成分ポリマーと添加ポリマーを混合割合で９０重量部：１０重量部に変更した後は同様の操作にて延伸糸を作成した。この際、重合物混合物の極限粘度[η]Mは１９．５であった。２段目の延伸が若干不調で延伸倍率を４倍に落さなければならなず、結果として強度・弾性率等が低下したが、全般的には満足の行く物性を有する繊維を得ることができた。

【００３１】（実施例４）実施例１において、ポリマーを溶解する際にブレンドポリマーの総量に対して１ｗｔ％の酸化防止剤（商標名「ヨシノックスＢＨＴ」吉富製薬製）を添加した他は同様の操作で延伸糸を得る実験を実施した。紡糸速度が３０ｍ／ｍｉｎまでが上限であったが、その後の延伸は比較的安定に実施可能であった。得られた繊維の特性は実施例１に比較して、特に粘弾性特性において低下したものの、全般的には満足の行く結果が得られた。

【００３２】（実施例５）実施例１において、主成分のポリマーをエチレンに対して１－オクテンを０．１mol％共重合させた極限粘度１８．２のポリマーを用いた他は同様の操作せ繊維を得た。尚、混合物の極限粘度は１８．５であった。実施例１に比べると繊維の弾性率が若干低下する傾向にあるが、紡糸での曳糸性および延伸での操業性等はむしろ優れる結果となった。動的粘弾性特性も非常に優れた結果となった。

【００３３】（比較例１）実施例１の主成分ポリマーのみを用い高分子量物は添加しなかった。紡糸直下での糸切れが甚だしく、満足の行く繊維を曳き取ることができなかった。

＊【００３４】（比較例２）実施例１に用いた主成分ポリマー（Ａ）を０．２重量％と、ポリマーに対して１ｗｔ％となるように酸化防止剤（商標名「ヨシノックスＢＨＴ」吉富製薬製）を添加してデカリンに均一溶解した後、平面状のガラス板にキャスティングして１昼夜自然に放置した後、８０℃の温度で真空下でさらに２昼夜かけて完全に溶剤を蒸発させて厚さ約１５ﾐｸﾛﾝのキャストフィルムを作成した。これを、加熱温度を設置した引張り試験機で約１０ｍｍ／ｍｉｎの歪み速度にて５０℃で４０倍、１２０℃で３倍さらに１４０℃で２倍の合計２４０倍延伸し、高度に配向したフィルムを作成した。得られたフィルムの強度を(g/d)表示に換算したものを表１にまとめる。フィルムの動的粘弾性測定は繊維の測定法にその試料寸法および厚みが準拠するように測定し実厚みで最終補正した。得られたフィルムの特性は、高強度・高弾性率で満足の行くものであった。特に、延伸倍率の高さにみられるように弾性率において特に優れた結果となった。一方、動的粘弾性特性ではγ分散の値は低いものの、そのピーク温度が非常に高温にシフトし、所望とする物性を得る事ができなかった。

【００３５】（比較例３）実施例１に用いた主成分ポリマーの替わりに極限粘度１８．８で分子量分布指数Ｍｗ／Ｍｎ＝８．５のポリマーを使用した他は同様の操作で延伸糸を得た。尚、ブレンド体の平均の極限粘度は１８．９であった。実施例１に比較して糸の延伸性が低下し若干延伸倍率を低下させる必要が生じその分、強度が低下した。動的粘弾性特性のγ分散の損失弾性率のピーク位置の温度は－１１６℃と良好であったが、その損失正接は０．０４０と大きな値となった。

【００３６】

＊ 【表１】

実験	[η]B (g/dl)	[η]F (g/dl)	延伸倍率	強度 (g/d)	弾性率 (g/d)	γ分散温度 (℃)	tanδ (－)
実施例1	18.8	15.2	18	43.1	1557	－114	0.021
実施例2	12.7	10.3	18	32.5	1025	－119	0.028
実施例3	19.6	16.3	16	45.2	1533	－112	0.025
実施例4	18.8	17.2	18	34.6	918	－111	0.029
実施例5	18.2	18.5	18	41.1	1235	－116	0.024
比較例1	18.5	－	－	－	－	－	－
比較例2	18.5	17.8	240	44.7	1905	－98	0.022
比較例3	18.9	15.5	17.5	33.5	1103	－116	0.040

【００３７】

【発明の効果】温度変化に対する繊維特性の変化が極めて少なく、常温での力学特性に優れる高強度ポリエチレン繊維を提供することを可能とした。

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(54) HIGH-STRENGTH POLYETHYLENE FIBER AND PROCESS FOR PRODUCING THE SAME

(57) A high-strength fiber having an intrinsic viscosity of 5 or higher, a strength of 20 g/d or higher, a modulus of 500 g/d or higher, and dynamic viscoelasticity in which the γ dispersion loss modulus peak temperature is 100 degrees or lower and the loss tangent is 0.03 or lower. This fiber, which changes little in material properties with changing temperature and has excellent ordinary-temperature mechanical properties, can be efficiently provided by stretching a fiber spun from a 5 to 80 % solvent solution of a mixture comprising 99 to 50 parts by weight of a high-molecular polyethylene polymer A having an intrinsic viscosity of 5 or higher and a weight-average molecular weight/number-average molecular weight ratio of 4 or lower and I to 50 parts by weight of an ultrahigh-molecular polymer B having an intrinsic viscosity at least 1.2 times that of the polymer A.

EP 1 193 335 A1

Description

Technical field

[0001] The present invention relates to high-strength polyethylene fibres which can be used in a wide range of fields, as various ropes, fishing lines, netting and sheeting for engineering, construction and the like, cloth and nonwoven cloth for chemical filters and separators, sportswear and protective clothing such as bulletproof vests, or as reinforcing material for composites for sport, impact-resistant composites and helmets, and particularly as various industrial materials used at from extremely low temperatures to room temperature; where the performance of said fibres, particularly the mechanical properties such as strength and elastic modulus, undergo little variation with temperature during use in environments subject to large changes in temperature; and the present invention relates to a method for producing said fibres sufficiently quickly industrially.

Background technology

[0002] In recent years, active attempts have been made to obtain high-strength, high-elastic modulus fibres from ultrahigh molecular weight polyethylene starting material, and extremely high strength/elastic modulus fibres have been reported. For example, Japanese Unexamined Patent Application S56-15408 discloses a technique known as the "gel spinning method", where gel-like fibres obtained by dissolving ultrahigh molecular weight polyethylene in solvent are drawn to a high draw ratio.

[0003] It is known that the high strength polyethylene fibres obtained by the "gel spinning method" are very high in strength and elastic modulus as organic fibres, and are also highly superior in terms of impact resistance, and these fibres are being evermore widely used in various fields. The abovementioned Japanese Unexamined Patent Application No. S56-15408 discloses that it is possible to provide a material having extremely high strength and elastic modulus, in order to obtain such high strength fibres. However, it is known that high strength polyethylene fibres undergo major changes in performance with temperature. For example, measuring the tensile strength while varying the temperature from about -160°C reveals a gradual decrease as the temperature increases, and that decrease in performance is particularly marked at from -120°C to around -100°C. With regard to temperature-related performance, then, it is anticipated that the performance of conventional high-strength polyethylene fibres could be considerably improved if their physical properties at extremely low temperatures could be maintained at room temperature.

[0004] Conventional attempts to control changes in the mechanical properties of high-strength polyethylene fibres due to changes in temperature include an attempt to improve the vibration absorption at temperatures not greater than -100°C (referred to as the extremely low temperature region) by using a suitable ultrahigh molecular weight polyethylene starting material of a specific molecular weight and keeping the molecular weight of the resulting fibres within a suitable range, as disclosed in Japanese Unexamined Patent Application No. H7-166414, but, fundamentally, that technique increases the mechanical dispersion at extremely low temperature. Specifically, it attempts to increase the variation in elastic modulus, whereas the present invention aims to lessen the deterioration in mechanical properties.

[0005] Japanese Unexamined Patent Application Nos. H1-156508 and H1-162816 disclose attempts to reduce the creep in high-strength polyethylene fibres by means such as ultraviolet irradiation and peroxides, in the abovementioned gel spinning method. It is noted that, fundamentally, this does decrease the mechanical dispersion in γ dispersion as described above, which is described in the present invention as desirable, but both inventions aim to improve the creep of high-strength polyethylene fibres, but do not decrease the variation in mechanical properties due to changes in temperature. Specifically, if the relaxation strength in the γ dispersion is smaller, the temperature at which the relaxation occurs is usually shifted higher, and so as it is desirable in the present invention to decrease the variation in mechanical properties that occur on changes in temperature, that is, to shift the γ dispersion temperature to a lower temperature, the conventional methods are contrary to the aim of the present invention.

[0006] Specifically, it is suggested that having a small γ dispersion value for γ dispersion temperatures in the range no greater than -100°C, as relaxation strength, while keeping the temperature region therefor at very low temperatures allows the good physical properties (especially strength) seen in the very low temperature region to be maintained without relaxation even for long periods at temperatures around room temperature, and such fibres would be extremely useful industrially. Fibres having such novel properties could, as described below, be substituted for conventional high-strength polyethylene fibres with no loss of the fundamental merits which said conventional fibres should have; moreover, as they are high-strength fibres, it is anticipated that they could also be drawn at extremely high speed during production processes and particularly during drawing processes. That is to say, this also has industrial significance as a novel production method which can yield high-strength polyethylene fibres of excellent performance at higher productivity.

[0007] In view of the situation described above, the present invention aims to provide high-strength polyethylene fibres characterized in that they have excellent mechanical properties at normal temperatures, and in that the mechan-

ical properties such as strength and elasticity modulus seen on wide temperature variation, particularly in the liquid nitrogen temperature region, are maintained at a high level even at room temperature; and a novel production method therefor.

Disclosure of the invention

[0008] The first invention of the present invention provides high-strength polyethylene fibres characterized in that they are polyethylene fibres comprising mainly ethylene component having an intrinsic viscosity [η], when fibrous, of no less than 5, and have a strength of no less than 20 g/d and an elasticity modulus of no less than 500 g/d, and, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -110°C and the loss tangent (tan δ) is no greater than 0.03.

[0009] The second invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -115°C.

[0010] The third invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss tangent (tan δ) is no greater than 0.02.

[0011] The fourth invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 100°C.

[0012] The fifth invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 105°C.

[0013] The sixth invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that they have a strength of no less than 25 g/d and an elasticity modulus of no less than 800 g/d.

[0014] The seventh invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that they have a strength of no less than 35 g/d and an elasticity modulus of no less than 1200 g/d.

[0015] The eighth invention of the present invention provides a method for producing high-strength polyethylene fibres, characterized in that a polymerization mixture comprising from 99 to 50 parts by weight of (A) and from 1 to 50 parts by weight of (B), where (A) is high molecular weight polymer comprising mainly ethylene component and having a weight average molecular weight to number average molecular weight ratio (Mw/Mn) of no greater than 4 and an intrinsic viscosity [η] of no less than 5, and (B) is an ultrahigh molecular weight polymer having an intrinsic viscosity at least 1.2 times that of high molecular weight polymer (A), is dissolved in solvent to a concentration of from 5% by weight to 80% by weight, then spun and drawn.

[0016] The ninth invention of the present invention provides a method for producing high-strength polyethylene fibres according to Claim 8, characterized in that the high molecular weight polymer (A) is a polyethylene polymer comprising mainly ethylene component having a weight average molecular weight to number average molecular weight ratio (Mw/Mn) of no greater than 2.5 and an intrinsic viscosity [η] of from 10 to 40.

[0017] The tenth invention of the present invention provides a method for producing high-strength polyethylene fibres according to Claim 8, characterized in that the average intrinsic viscosity [η]M of the polymerization mixture is no less than 10 and the intrinsic viscosity [η]F of the resulting fibres satisfies the formula below

$$0.6 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

[0018] The eleventh invention of the present invention provides a method for producing high-strength polyethylene fibres according to Claim 8, characterized in that the intrinsic viscosity [η]F of the resulting fibres satisfies the formula below

$$0.7 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

[0019] The working mode of the present invention is described below.

[0020] The high molecular weight polyethylene of the present invention is characterized in that its repeat unit is essentially ethylene, although it may be a copolymer thereof with small amounts of other monomers such as α-olefin, acrylic acid or derivatives thereof, methacrylic acid or derivatives thereof or vinyl silane or derivatives thereof, or it may be a copolymer with these, or a copolymer with ethylene homopolymer, or it may be a blend with homopolymers of other α-olefins and the like. The use of a copolymer with an α-olefin such as propylene or butene-1 is particularly

preferred in that a degree of short or long chain branching imparts stability during the production of these fibres, particularly during spinning and drawing. However, too high a content of components other than ethylene has an adverse effect on drawing, and so in order to obtain fibres of high strength and high elasticity modulus, the monomer unit content should be no greater than 5 mol%, and is preferably no greater than 1 mol%. Obviously, homopolymer comprising ethylene alone may be used.

[0021] The characterizing feature of the present invention is, in essence, the provision of fibres characterized in that, in the temperature variance of the dynamic viscoelasticity properties measured when fibrous, the γdispersion loss modulus peak temperature is no greater than -110°C, preferably no greater than -115°C, and the value of the loss tangent thereof (tan δ) is no greater than 0.03, preferably no greater than 0.02, and that the crystalline α dispersion loss modulus peak temperature is not less than 100°C, preferably not less than 105°C. The present invention also provides a method for obtaining fibres having these properties, that is, a method for producing high-strength polyethylene capable of essentially high speed drawing, at far higher productivity than conventional methods for producing the same kind of fibres.

[0022] The decrease in the temperature-dependent variation in the properties of the inventive fibres, particularly the excellent mechanical properties (particularly strength) at room temperature, can be defined in terms of the fibres' dynamic viscoelastic crystalline α dispersion peak temperature and γ dispersion peak temperature. Specifically, a marked decrease in elasticity modulus is usually seen in the temperature region in which mechanical dispersion occurs. In the case of high-strength polyethylene fibres, γ dispersion is usually observed around -100°C. At and beyond the limits of this γ dispersion, the physical values of polyethylene decrease markedly as the temperature is increased towards room temperature. For example, polyethylene fibres which are very strong (4 GPa) in an extremely low temperature atmosphere obtained using liquid nitrogen or the like (approximately -160°C) are less strong (their strength decreases to approximately 3 GPa) when measured at room temperature. Such an effect is obviously undesirable in products which involve the use of said fibres in wide temperature ranges, and it is thought that if this phenomenon could be improved upon, it would be possible to drastically improve strength at room temperature.

[0023] Moreover, high-strength polyethylene fibres exhibit a crystalline α dispersion at around 85°C, and even in this temperature region there is considerable variation in elastic modulus and strength, which is undesirable for various products. Accordingly, in order to allow a certain margin, the temperature range for the use of these fibres is usually decided by setting a temperature range between the γ dispersion temperature and the crystalline αdispersion temperature.

[0024] The lowering of the γ dispersion temperature and the raising of the crystalline αdispersion temperature is therefore highly significant in that it widens the abovementioned temperature range for use.

[0025] The γ dispersion is the first point scrutinized when aiming to develop new fibres based on this ideal design, and it is known that this γ dispersion originates from local defects at side chains, terminals and the like in the molecules which make up the fibres. Decreasing the number of defects would decrease the γdispersion relaxation strength (that is, the loss tangent (tan δ)), but this would usually result in a more perfect fibre-fine structure, and so the temperature at which γ dispersion occurs would automatically shift to a higher temperature. Moreover, the crystalline α dispersion peak temperature in the present fibres is very high (at least 100°C or more, preferably 105°C or more) compared to that of conventional high-strength polyethylene fibres obtained by the abovementioned means such as drawing (which is at most 95°C). Furthermore, even if the abovementioned fibres which have a high crystalline αdispersion are excluded, it is difficult to achieve a temperature lower than -110°C in γ dispersion for highly crystalline fibres which usually have a crystalline α dispersion temperature of at least 90°C. Some fibres, for example those having a crystalline α dispersion temperature of around 85°C, do exhibit γ dispersion temperatures at or lower than -110°C, but this is because their fibre structure has become more amorphous, and such fibres are clearly distinguishable from the novel fibres targeted by the present invention, which have a high crystallinity (a high crystalline α dispersion temperature) and a low γ dispersion temperature.

[0026] Contrary to conventional technology, it is absolutely impossible to decrease the relaxation strength while the γ dispersion peak temperature is kept low. Given conventional common-sense, it is extremely surprising that the γ dispersion peak temperature in the fibres provided by the present invention is kept very low and that the value thereof is extremely small.

[0027] The means for obtaining the fibres of the present invention is necessarily a novel and cautious method. Moreover, the means described below provides high-strength polyethylene fibres of the present invention which also have the general characteristics of conventional high-strength polyethylene and so said means is also valuable industrially as a novel production method for these which achieves very high productivity.

[0028] The fibres of the present invention are obtained efficiently in practice by the abovementioned "gel spinning method", although provided that ultrahigh molecular weight polyethylene is moulded to yield known high-strength polyethylene fibres, any standard spinning technique may be used. The starting material polymer is of first importance in the present invention.

[0029] Specifically, the present invention recommends the use of a polymerization mixture of at least two types of

ultrahigh molecular weight polyethylene, comprising from 99 to 50 parts by weight of (A) and from 1 to 50 parts by weight of (B), where (A) is high molecular weight polymer comprising mainly ethylene component having a weight average molecular weight to number average molecular weight ratio (Mw/Mn) of no greater than 4 and an intrinsic viscosity [η] of no less than 5, and (B) is an ultrahigh molecular weight polymer having an intrinsic viscosity at least 1.2 times that of high molecular weight polymer (A). Above all, polymer (A) should have an intrinsic viscosity of no less than 5, preferably no less than 10, but not more than 40, and the Mw/Mn of the polymer, measured by GPC (gel permeation chromatography), should be no greater than 4, preferably no greater than 3, and more preferably no greater than 2.5.

[0030] First, in order to achieve the inventive low value for the γ dispersion temperature, it is necessary to select a substance with as few defects as possible on the branches, terminals and the like, and so the degree of polymerization of the main polymer (A) is important, and if the intrinsic viscosity is less than 5, the molecular terminals increase considerably and the γ dispersion tan δ value increases. If it exceeds 40, however, the viscosity of the solution becomes too great during spinning and spinning becomes difficult. Here, the average molecular weight (which represents intrinsic viscosity) and the distribution thereof, that is, the molecular weight distribution, are very important, and the Mw/Mn (measured by GPC) is preferably no greater than 4. By using a starting material which has an ultrahigh molecular weight and has a relatively uniform molecular weight distribution, it is easy to maintain a low γ dispersion temperature and have a low tan δ value thereof.

[0031] The reason for this is not well understood, although it is speculated that when the molecular chain is made uniform, crystals (thought to be formed by the extending of the chains) cause the molecules to line up and become oriented, and so there are very few molecular terminals in the crystalline region, and the molecular terminals collect and remain in the so-called amorphous region. That is, it is speculated that the crystalline region, which makes up most of the inventive fibre structure, becomes more perfectly crystalline, with fewer defects, and the components such as molecular terminals concentrate in the amorphous region. This corresponds with the scientifically known fact that if the crystalline region contains many defects (which dictate the γ dispersion), the peak temperature will shift to a higher temperature, and with the fact that there are few local regions of molecular terminals and the like in the crystalline part of fibres of the present invention. As the main structure of the inventive fibres is a crystalline structure comprising extended chains, it is thought that the molecular terminals concentrate in the amorphous part and do not particularly affect physical properties, although this is a hypothesis contrived to explain the effects of the present invention and is not certain.

[0032] Thus by merely using an ultrahigh molecular weight polyethylene polymer having an extremely narrow molecular weight distribution in a common spinning method, stable discharge cannot be achieved during spinning because the molecular weight distribution of the starting material polymer is very narrow, and the discharged solution has almost no extendability and so moulding it is impossible in practice. The molecular weight distribution Mw/Mn should at least be greater than 4 when an abovementioned polymer is supplied to a conventional gel spinning method. An example of an attempt to use such a low molecular weight polymer is disclosed in Japanese Unexamined Patent Application No. H9-291415, wherein high strength, high elasticity modulus fibres are obtained using an ultrahigh molecular weight polyethylene-based polymer that is prepared using a special catalyst and has a viscosity average molecular weight of no less than 300,000 and an Mw/Mn ratio of no greater than 3. According to said publication, the technique disclosed therein is commonly employed, rather than the gel spinning method which is commonly used to produce high-strength polyethylene fibres; said disclosed technique involves a combination of solid phase extrusion and gel extension using a dry simple crystal aggregate reagent, where said simple crystal aggregate is obtained by dissolving polymer to a dilute solution of a concentration of no more than 0.2 wt%, and technology involving the use of a simple crystal aggregate is also disclosed in the working example. As shown in this example, it is extremely difficult to perform spinning and drawing processes using the low Mw/Mn polymer of the conventional gel spinning method. Needless to say, the general properties and physical properties of the gel drawn films made from the very dilute solutions disclosed in said publication are different from those of the novel fibres provided by the present invention.

[0033] The reason why it is difficult to mould such polymers having a very narrow molecular weight distribution is perhaps that the intertwining of molecular chains is drastically reduced as a result of the narrow molecular weight distribution, and so the stress required to deform the molecular chains during spinning and drawing cannot be uniformly transmitted, although this is merely speculation. With this in mind, diligent research was performed into improving conventional technology, and the present invention was achieved on discovering that the use of a mixture comprising from 99 to 50 parts by weight of polymer (A) (main component) and from 1 to 50 parts by weight of ultrahigh molecular weight polymer (B) having an intrinsic viscosity that is at least 1.2 times that of polymer (A) greatly facilitates spinnability (facilitates take-up when the solution discharged from the spinneret is drawn) and drawing, and markedly improves drawing speed, and the resulting fibres have the required properties described above, that is, the γdispersion temperature is low and tan δ is low. Furthermore, in the present invention, by using a mixture in which the average intrinsic viscosity [η]M of the polymers therein is not less than 10, and by dissolving the polymer in solvent so that it comprises from 5% by weight to 80% by weight of the total, and spinning and drawing under production conditions so that the

intrinsic viscosity [η]F of the resulting fibres satisfies the equation below, it is possible to obtain fibres having physical properties that are remarkably close to those desired:

$$0.6 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

preferably,

$$0.7 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

[0034] It is not certain how this relationship between the molecular weight of the starting material polymers and the resulting fibres affects the physical properties of the fibres, but if the intrinsic viscosity [η]F of the fibres exceeds 90% of [η]M, the two different molecular weight polymers do not uniformly mix and extendability is extremely poor, whereas if [η]F is less than 70% of [η]M, mixing two polymers has almost no effect and it is only possible to achieve more or less the same physical properties as seen in high strength polyethylene fibres in which the molecular weight distribution is as wide as usual. A large difference between the degree of polymerization of the resulting fibres and the starting material polymer means that the molecular chains break during processing, and the molecular weight distribution has to be somehow readjusted. It has been suggested that at this time the polymer of high molecular weight within the mixture often deteriorates more, and that by adjusting the molecular weight distribution of the whole so that this high molecular weight matter is incorporated in the low molecular weight matter molecular weight distribution region, a smoother molecular sequence is obtained, and, as the residual high molecular weight component fulfils its role of spreading tension during moulding, both mouldability and workability during spinning and drawing are achieved, although this is speculation and has not been confirmed.

[0035] Fibres obtained by the abovementioned methods have an intrinsic viscosity [η]F, when fibrous, of no less than 5, preferably from 10 to 40, a strength of no less than 20 g/d, preferably no less than 25 g/d, and more preferably no less than 35 g/d, and an elastic modulus of no less than 500 g/d, preferably no less than 800 g/d, more preferably no less than 1200 g/d, and, as a result of synergistic effects with mechanical dispersion properties as described above, it is possible to provide polyethylene fibres of excellent properties for practical use, which are not known conventionally.

Optimum mode of the present invention

[0036] The present invention is described below by means of working examples, but the present invention is not limited to these.

[0037] The measurement methods and measurement conditions for the property values in the present invention are described first.

Dynamic viscoelasticity measurement

[0038] In the present invention, dynamic viscosity was measured using a Rheoviblon DDV-01FP, manufactured by Orientec. The fibres as a whole were divided or doubled to have 100 denier ± 10 denier, and while the respective fibres were arranged as uniformly as possible, both the terminals of the fibres were enclosed with aluminium foils such that the measurement length (distance between the chuck ends) was 20 mm, and the fibres were adhesive-bonded with a cellulose type adhesive. The length of the margin left for applying the adhesive was made around 5 mm to allow fixing of the chuck. Each test sample was set carefully on the chuck at an initial width of 20 mm to prevent the strand from being entwined or twisted around it, then the fibres were subjected to preliminary deformation for a few seconds at a temperature of 60°C and a frequency of 110 Hz. In this experiment, the temperature distribution was determined at a frequency of 110 Hz in the range of from -150°C to 150°C, increasing the temperature from -150°C at a rate of approximately 1°C/min. During measurement, the stationary load was set at 5 gf and the sample length was automatically controlled to prevent the fibres from loosening. The dynamic deformation amplitude was set at 15 μm.

Strength/elastic modulus

[0039] In the present invention, the strength and elastic modulus of a 200 mm-long sample were determined using Tensilon, manufactured by Orientec, at a draw rate of 100%/min, and the distortion-stress curve was obtained at an atmospheric temperature of 20°C and 65% relative humidity; the stress (g/d) at the break point in the curve was determined, and the elastic modulus (g/d) was calculated from the tangent of the line giving the maximum slope in the vicinity of the origin of the curve. Each value was the average of 10 measurements.

Intrinsic viscosity

[0040] The relative viscosities of various dilute solutions in decalin at 135°C were measured using an Ubbellohde type capillary viscosity tube, and the intrinsic viscosity was determined from the extrapolation point towards the origin of the straight line obtained by least square approximation of plots of viscosities against concentration. For these measurements, if the starting material polymer was powdery it was used in that form without further modification, whereas in the case of lumpy powder or fibrous samples, solutions for measurement were prepared by dividing or cutting the samples to approximately 5 mm in length, adding antioxidant (Yoshinox BHT, manufactured by Yoshitomi Seiyaku) at 1 wt% with respect to the polymer, then dissolving with agitation for 4 hours at 135°C.

Molecular weight distribution measurement

[0041] For this patent, Mw/Mn was measured by the gel permeation chromatography method. Measurements were made at a temperature of 145°C using a 150C ALC/GPC instrument manufactured by Waters, and GMHXL series column manufactured by Tosoh (K.K.). The calibration curve for the molecular weight was obtained using a polystyrene high molecular weight calibration kit manufactured by Polymer Laboratories. The sample solutions used were obtained by dissolving in trichlorobenzene to 0.02 wt%, adding antioxidant (Irgafos 168, manufactured by Ciba Geigy) at 0.2 wt% of the polymer, then dissolving for approximately 8 hours at 140°C.

[0042] The present invention is described in detail below.

Working Example 1

[0043] A powder mixture comprising 99 parts of homopolymer (A) of ultrahigh molecular weight polyethylene having an intrinsic viscosity of 18.5 and a molecular weight distribution index Mw/Mn of 2.5 and 2 parts by weight of polymer (D) having an intrinsic viscosity of 28.0 and a molecular weight distribution Mw/Mn of approximately 5.5 was taken, and 70% by weight of decahydronaphthalene was added at normal temperature so that said mixture made up 30% by weight of the total. At this time, the intrinsic viscosity [η]M of the polymer mixture was 18.8. A decalin dispersion of this mixed polymer was supplied to a twin-screw mixer/extruder and dissolved and extruded at 200°C and 100 rpm. It should be noted that antioxidant was not used at that time .

[0044] Solution prepared in this way was extruded using a spinneret provided with 48 holes of orifice 0.6 mm in diameter such that the output from each hole was 1.2 g/min, then part of the solvent was immediately removed using inert gas adjusted to room temperature, and the sample was taken off at a rate of 90 m/min. Immediately after having been taken off, the polymer content of the gel-like fibres was 55% by weight. This yarn that had been taken off was immediately drawn 4-fold in a 120°C oven, then wound once, then further drawn 4.5-fold in an oven adjusted to 149°C, to yield high-strength fibres. The various physical properties, including the dynamic viscoelasticity, of the resulting fibres are shown in Table 1.

Working Example 2

[0045] Spun yarn was obtained by the same operations as in Working Example 1, except that polymer having an intrinsic viscosity of 12.0 was used as the main component polymer. At this time, the intrinsic viscosity [η]M of the polymer mixture was 10.6. Drawing was much smoother than in Working Example 1, but the strength of the resulting fibres was slightly lower.

Working Example 3

[0046] The proportion of the main component polymer of Working Example 1 and the added polymer was adjusted to 90 parts by weight: 10 parts by weight, then spun yarn was obtained by the same operations. At this time, the intrinsic viscosity [η]M of the polymer mixture was 19.5. The second drawing was slightly awkward and the draw ratio had to be dropped to 4-fold, and as a result the strength and elasticity modulus and the like were lower, although it was possible to obtain fibres having physical properties which were satisfactory overall.

Working Example 4

[0047] An experiment was performed which involved obtaining spun yarn by the same operations as in Working Example 1, except that when the polymer was dissolved, antioxidant (trade name Yoshinox BHT, manufactured by Yoshitomi) was added at 1 wt% with respect to the total amount of blend polymer. The spinning speed was increased to an upper limit of 30 m/min, and thereafter relatively stable drawing was possible. The properties of the resulting

fibres were compared with those achieved in Working Example 1, and although the elasticity in particular was lower, overall satisfactory results were obtained.

Working Example 5

[0048] Fibres were obtained by the same operations as in Working Example 1, except that polymer having an intrinsic viscosity of 18.2 obtained by copolymerizing 1-octene at 0.1 mol% with respect to ethylene was used as the main component polymer. It should be noted that the intrinsic viscosity of the mixture was 18.5. the elasticity of the fibres tended to be slightly lower than those obtained in Working Example 1, although when it came to spinning, the spinnability and the workability on extension and the like were superior. The dynamic viscoelasticity was also excellent.

Comparative Example 1

[0049] Only the main component polymer of Working Example 1 was used, and no high molecular weight material was added. Spinning resulted in immediate serious yarn breakage and it was impossible to pick up satisfactory fibres.

Comparative Example 2

[0050] 0.2% by weight of main component polymer (A) used in Working Example 1 were taken, antioxidant (trade name Yoshinox BHT, manufactured by Yoshitomi) was added to 1 wt% with respect to the polymer, and these were dissolved uniformly in decalin, then casting was performed on a flat surface glass plate which was then left naturally overnight, then the solvent was completely evaporated off by leaving the system in a vacuum at 80°C over 2 nights, to yield an approximately 15 micron thick cast film. This was drawn 4-fold at 50°C, 3-fold at 120°C and then 2-fold at 140°C to a total of 240-fold at a distortion speed of approximately 10 mm/min using a tension tester with provision for high temperatures, to yield a highly oriented film. The strength of the resulting film, calculated as (g/d) is shown in Table 1. The dynamic viscoelasticity of the film was measured by measuring according to the measurement method for fibres corresponding to the dimensions and thickness of the sample, then performing final correction to the actual thickness. The properties of the resulting film were such that it had sufficient high strength and high elasticity modulus. Specifically, the elasticity modulus was particularly excellent, as seen from the high draw rate. As for its dynamic viscoelasticity, although the γ dispersion value was low, its peak temperature shifted to an extremely high temperature and it was impossible to achieve the desired physical properties.

Comparative Example 3

[0051] Drawn yarn was obtained by the same operations except that polymer having an intrinsic viscosity of 18.8 and a molecular weight distribution index Mw/Mn of 8.5 was used instead of the main component polymer used in Working Example 1. It should be noted that the average intrinsic viscosity of the blend was 18.9. the yarn extendability was less than that achieved in Working Example 1 and it was necessary to decrease the draw ratio slightly, and so the strength was lower. As for the dynamic viscoelasticity, the γ dispersion loss modulus peak value temperature was good, at -116°C, although the loss tangent was a high value, at 0.040.

Industrial uses

[0052] It is possible to provide high-strength polyethylene fibres which can be used in a wide range of fields, as various ropes, fishing lines, netting and sheeting for engineering, construction and the like, cloth and nonwoven cloth for chemical filters and separators, sportswear and protective clothing such as bulletproof vests, or as reinforcing material for composites for sport, impact-resistant composites and helmets, and particularly as various industrial materials used at from extremely low temperatures to room temperature; where the properties of the fibres change very little with temperature variation and where said high-strength polyethylene fibres have excellent mechanical properties at normal temperature. It is also possible to provide a method for producing these high-strength polyethylene fibres with sufficiently quickly speed industrially.

Table 1

Experiment	[η]B (g/dl)	[η]F (g/dl)	Draw rate	Strength (g/d)	Elasticity modulus (g/d)	γ dispersion temperature (°C)	tan δ (-)	Crystalline α dispersion temperature (°C)
Working Example 1	18.8	15.2	18	43.1	1557	-114	0.021	110
Working Example 2	12.7	10.3	18	32.5	1025	-119	0.028	105
Working Example 3	19.6	16.3	16	45.2	1533	-112	0.025	112
Working Example 4	18.8	17.2	18	34.6	918	-111	0.029	107
Working Example 5	18.2	18.5	18	41.1	1235	-116	0.024	108
Comparative Example 1	18.5	-	-	-	-	-	-	-
Comparative Example 2	18.5	17.8	240	44.7	1905	-98	0.022	95
Comparative Example 3	18.9	15.5	17.5	33.5	1103	-116	0.040	83

Claims

1. High-strength polyethylene fibres **characterized in that** they are polyethylene fibres comprising mainly ethylene component having an intrinsic viscosity [η], when fibrous, of no less than 5, and have a strength of no less than 20 g/d and an elasticity modulus of no less than 500 g/d, and, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -110°C and the loss tangent (tan δ) is no greater than 0.03.

2. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -115°C.

3. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss tangent (tan δ) is no greater than 0.02.

4. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 100°C.

5. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 105°C.

6. High-strength polyethylene fibres according to Claim 1, **characterized in that** they have a strength of no less than 25 g/d and an elasticity modulus of no less than 800 g/d.

7. High-strength polyethylene fibres according to Claim 1, **characterized in that** they have a strength of no less than 35 g/d and an elasticity modulus of no less than 1200 g/d.

8. Method for producing high-strength polyethylene fibres, **characterized in that** a polymerization mixture comprising from 99 to 50 parts by weight of (A) and from 1 to 50 parts by weight of (B), where (A) is high molecular weight polymer comprising mainly ethylene component and having a weight average molecular weight to number average molecular weight ratio (Mw/Mn) of no greater than 4 and an intrinsic viscosity [η] of no less than 5, and (B) is an ultrahigh molecular weight polymer having an intrinsic viscosity at least 1.2 times that of high molecular weight polymer (A), is dissolved in solvent to a concentration of from 5% by weight to 80% by weight, then spun and drawn.

9. Method for producing high-strength polyethylene fibres according to Claim 8, **characterized in that** the high molecular weight polymer (A) is a polyethylene polymer comprising mainly ethylene component having a weight average molecular weight to number average molecular weight ratio (Mw/Mn) of no greater than 2.5 and an intrinsic viscosity [η] of from 10 to 40.

10. Method for producing high-strength polyethylene fibres according to Claim 8, **characterized in that** the average intrinsic viscosity [η]M of the polymerization mixture is no less than 10 and the intrinsic viscosity [η]F of the resulting fibres satisfies the formula below

$$0.6 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

11. Method for producing high-strength polyethylene fibres according to Claim 8, **characterized in that** the intrinsic viscosity [η] F of the resulting fibres satisfies the formula below

$$0.7 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/02766

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[6] D01F6/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[6] D01F6/46

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999
Kokai Jitsuyo Shinan Koho 1971-1995 Jitsuyo Shinan Toroku Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 1-156508, A (Toray Industries,Inc.), 20 June, 1989 (20. 06. 89) (Family: none)	1-7
A	JP, 1-162819, A (Toray Industries,Inc.), 27 June, 1989 (27. 06. 89) (Family: none)	8-11
A	JP, 7-166414, A (Toyobo Co., Ltd.), 27 June, 1995 (27. 06. 95) & US, 5443904, A	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

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